PRODUCTION AND UTILIZATION OF POROUS HOLLOW EPOXY BY WATER-BASED METHOD AS AN ADVANCED FILLER

by

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DEDICATION

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12F-PE	Fluorinated poly(aryl eher ketone)
AFM	Atomic force microscope
AIBN	2,2 –azobisisobutyronitrile
Al_2O_3	Aluminum oxide
AN	Monomeric Acrylonitrile
ASP	Alkali Swelling Procedure
ATBN	Amine-terminated butadiene-acrylonitrile
BA	Butyl acrylate
BET	Brunauer, Emmett & Teller (1938)
BHT	2,6-di-tert-butyl-p-cresol
BPO	Benzoyl peroxide
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
CIPS	Chemically Induced Phase Separation
CNT	Carbon nanotube
CO_2	Carbon dioxide
CTBN	Carboxyl-terminated butadiene-acrylonitrile
DEGDA	Diethylene glycol diacrylate
DETA	Diethylenetriamine
DGEBA	Diglycidyl ether of bisphenol A
DLA	Diffusion-limited aggregate
DNA	Deoxyribonucleic acid
DPP	Diphenylolpropan

DRC	Dry rubber content
DSC	Differential Scanning Calorimetry
DSM	Dynamic Swelling Method
ECH	Epichlorohydrin
eew	epoxide equivalent weight
EGDMA	ethylene glycol dimethacrylate
ENR	Epoxidised natural rubber
EPDM	Ethylene Propylene Diene rubber
ETBN	Epoxy-terminated butadiene-acrylonitrile rubber
FTIR	Fourier transform infrared spectroscopy
GPC	Gel Permeation Chromatography
HBPs	Dendritic hyperbranched polymers
HCl	Hydrochloride acid
IPN	A semi-interpenetrating polymer network
KOH	Potassium hydroxide
LCD	Liquid crystal display
LLDPE	Linear low density polyethylene
LS	Pristine layer silicate
MAA	Methacrylic acids
MBT	2-mercapto-benzothiazole
$MgSO_4$	Magnesium sulfate
MMA	Methyl methacrylate
MMT	Montmorillonite
MTEOS	$CH_3Si(OC_2H_5)_3$ - Methyl triethyl orthosilicate
Na_2HPO_4	Sodium hydrogen phosphate

Na_2SO_4	Sodium sulfate
NaCl	Sodium chloride
$NaHSO_3$	Sodium sulfite
NaOH	Sodium hydroxide
NH_3	Ammonia
NH_4OH	Ammonium hydroxide
NR Latex	Natural rubber latex
NR	Natural rubber
O/W	oil-in-water
O/W/O	oil-in-water-in-oil
OLS	Organophilic layer silicate
OP10	Rapeseed oil
P(S-MAA)	Styrene-methacrylic acid copolymer
PBA	Polybutylacrylate
PBT	Poly(butadiene terephthalate)
PC	Poly(carbonate)
PCL	Poly(ε-carprolactone)
PEEK	Poly(ether ether ketone)
PEI	Poly(ether imides)
PEO	Poly(ether oxide)
PEPO	Polyether-phosphineoxide
PES	Poly(ether sulfones)
PET	Polyethylene terephthalate
PI	Polyimide
PMMA	Poly(methyl methacrylate)

PPE	Poly (2,6-dimethyl-1,4-phenylene ether)
PPE	Poly(2,6-dimethyl-1,4-phenylene ether)
PPO	Poly(phenyl oxide)
PS	Polystyrene
PTEOS	$C_5H_6Si(OC_2H_5)_3$ - Phenyl triethyl orthosilicate
PU	Poly(urethane)
PVA	Poly (vinyl alcohol)
SaPSeP	Safe-assembling of Phase Separated Polymer
SBR	Styrene-Butadiene-Rubber
SC CO_2	supercritical carbon dioxide
SDBS	Sodium Dodecyl Benzene Sulfonate
SEM	Scanning Electron Microscope
SiO_2	Silicon dioxide
SMR	Standard Malaysian Rubber
SPG	Shirasu Porous Glass
TEM	Transmission electron microscopy
TEOS	$Si(OC_2H_5)_4$ - Tetraethyl orthosilicate
TGA	Thermogravimetric analysis
TMOS	$Si(OCH_3)_4$ - Tetramethyl orthosilicate
TMTD	Tetramethyl thiuram disulphide
TOFAS	Tall oil fatty acids
TPs	Thermoplastics
W/O	water-in-oil
W/O/W	water in oil in water
wpe	weight per epoxide
XRD	X-ray diffraction
ZnO	Zin oxide

PENGHASILAN DAN PENGGUNAAN EPOKSI BERLIANG GERONGGANG DENGAN KAEDAH BERASASKAN AIR SEBAGAI PERNGISI TERMAJU

ABSTRAK

Epoksi berliang geronggang (PHE) telah dihasilkan melalui kaedah berasaskan air dan digunakan sebagai pengisi di dalam polimer bagi meningkatkan "sifat-sifat bersama" pengisi dalam komposit. PHE telah dihasilkan dengan membenarkan ketidaklengkapan cantuman titisan kecil epoksi dalam emulsi, yang mana disediakan melalui penghomogenan campuran epoksi, poliamida dan kalsium karbonat dalam air. Partikel epoksi ini selepas dimatangkan adalah poros, berongga dan berbentuk seperti sfera. Lubang pada partikel epoksi boleh diisi dengan matrik polimer untuk membentuk pengikatan antara partikel epoksi dan polimer. Pengikatan ini menjamin interaksi yang lebih baik dan pengigi ini berpontensi untuk digunakan sebagai pengisi penguat. Mekanisma pengikatan ini adalah suatu konsep yang baru dan "novel".

Untuk penyediaan komposit, tiga jenis polimer yang akan digunakan sebagai matrik telah dipilih: Elastomer: lateks NR, NR, dan ENR; termoset: poliamina termatang epoksi ; termoplastik; LLDPE, PS dan PMMA. Keputusan menunjukkan pengikatan telah diperolehi untuk semua matrik polimer yang digunakan. Polimer yang berbeza akan menghasilkan mod kegagalan yang berbeza terhadap pengikatan. Secara am, terdapat tiga mod kegagalan dicadangkan, yang mana telah diklasifikasikan sebagai tertarik keluar (kekalkan morfologi *interlocked* dan ubahbentuk morfology *interlocked*) pemutusan matrik pada leher pengikatan dan pemutusan PHE. Pengikatan juga mempengaruhi sifat termal komposit. Komposit boleh menahan haba dengan baik memandangkan epoksi adalah bahan rintangan haba yang baik kerana ia mempunyai rangkaian sambung silang tiga dimensi. PHE

boleh mempengaruhi pergerakan rantai polimer dan ini memberi kesan terhadap pengurangan suhu peralihan kaca termoplastik (LLDPE, PS dan PMMA).

Pempolimeran in-situ dijalankan untuk menyelidik kesan PHE terhadap suspensi stirena/metil metakrilat (MMA) juga untuk proses sol-gel. Pengikatan melalui lubang epoksi antara PHE dan PS/PMMA adalah berjaya diperolehi melalui mikrograf SEM. PHE telah didapati bertindak balas dengan BPO dan membantu pempolimeran stirena dan MMA. Tambahan lagi, kesan PHE telah dilihat ke atas pempolimeran MMA dengan memberi kesan terhadap berat molekul berbeza yang diperolehi pada dalam dan luar lubang epoksi. Walaubagaimanapun, kesan adalah tidak begitu jelas untuk pempolimeran stirena disebabkan ketidakpolarannya. Untuk proses sol-gel, keputusan TGA mempamerkan kandungan silika yang sama ditinggalkan oleh PHE dan sampel PHE *interlocked*, jadi boleh dikatakan PHE mempunyai kesan sangat rendah kepada proses sol-gel.

Kesan saiz partikel dan morfologi lubang PHE terhadap pempolimeran suspensi MMA dan pencampuran leburan dengan PMMA telah diselidik. Penggunaan PHE yang sedikit memberikan kesan dalam peningkatan berat molekul PMMA diperolehi. Walaubagaimanapun , sifat termal tidak menunjukkan perbezaan yang ketara. Untuk komposit percampuran leburan PMMA, keputusan adalah menarik iaitu partikel PHE yang besar menunjukkan sifat tensil yang sedikit meningkat. Terdapat tiga jenis PHE dalam saiz 38-53 μm, 53-75 μm dengan kurang lubang, dan 75-106 μm dengan lubang berganda. Partikel penguat optimum adalah pada saiz 53-75 μm. Boleh dibuat kesimpulan bahawa PHE dengan bilangan lubang yang optimum dan saiz lubang yang optimum boleh menjadi pengisi penguat yang bagus, dimana ia dapat perbaiki semua sifat tensil seperti kekuatan tensil, pemanjangan pada takat putus begitu juga modulus.

PRODUCTION AND UTILIZATION OF POROUS HOLLOW EPOXY BY WATER-BASED METHOD AS AN ADVANCED FILLER

ABSTRACT

Porous hollow epoxy - PHE was produced by water based method and used as filler in polymer in order to improve the “collaborative properties” of filler in composites. The PHE was produced by allowing the incomplete coalescence of epoxy tiny droplets in emulsion, which was prepared by homogenizing the mixture of epoxy, polyamide and calcium carbonate in water medium. These epoxy particles after cured are porous, hollow and spherical. The holes on epoxy particle could be filled by the polymer matrix to form interlocking between epoxy particle and polymer. The interlocking should be promising better interaction and has potential to be used as reinforcing fillers. This interlocking mechanism is a new and novel concept.

To prepare composites, the polymer used as matrix were chosen in three types: elastomers: NR latex, NR and ENR; thermoset: epoxy cured polyamine; thermoplastic: LLDPE, PS and PMMA. The results showed the interlocking was obtained for all of the used polymer matrix. The mechanical properties were maintained or enhanced depending on the used polymer. Different polymer would result in different failure modes of the interlocking. In general, there are three proposed failure modes, which were classified as pulling out (maintain interlocked morphology and deform interlocked morphology), matrix broken at interlocking neck, and PHE broken. The interlocking was also effect thermal properties of composites. Composite could endure better heat since epoxy is a good heat resistance material due to its three dimension crosslink networks. PHE could affect to polymer

chain mobility resulting in slight reduction of glass transition temperature of thermoplastic (LLDPE, PS and PMMA).

In-situ polymerization was carried out to investigate the effect of PHE on suspension of styrene/methyl methacrylate (MMA) as well as sol-gel process. The interlocking through epoxy holes between PHE and PS/PMMA was successfully obtained as SEM photo of cutting surface pPS-PHE and pPMMA-PHE beads. PHE had found to react with BPO and retard the polymerization of styrene and MMA. Moreover, the effect of PHE had found on polymerization of MMA reflecting on different molecular weight obtained at inner and outer epoxy hole's. However, the effect could not be apparent for styrene polymerization due to its non polarity. For sol-gel process, TGA results exhibited a similar portion of silica remained of non PHE and interlocked PHE samples, so it could be said that PHE could have very low effect to sol-gel process.

The effect of particle size and hole's morphology of PHE on suspension polymerization of MMA and melt blending with PMMA was investigated. The use of smaller PHE resulted in higher molecular weight of PMMA obtained. However, thermal properties did not show an obvious difference. For PMMA melt blending composites, it is interesting that larger PHE particle expressed slightly higher tensile properties. There are three types of PHE in the size of 38 – 53 μm, and 53 – 75 μm with less holes, and 75 – 106 μm with multiple holes. It could be said that they are small particle with less medium holes, medium particle with medium holes, and large particle with many small holes. The optimum reinforcement particle is 53 – 75 μm. It concluded that a PHE with optimum number of holes and optimum hole's size would be a good reinforced filler, which improved better all tensile properties such of tensile strength, elongation as well as modulus.

CHAPTER 1

INTRODUCTION

1.1 Overview

The incorporation of filler into polymer to prepare a desired composite is the most attractive investigation for plastic applications. Composite properties would usually be tailored based on their filler properties. In general, two categories of filler properties are of interest in filled composites: “collaborative properties” and “self properties”. “Collaborative properties” influence dispersion and interaction of filler to matrix including surface features and morphology of filler, whilst “self properties” are additional properties obtained by the resultant composites such as mechanical, thermal, conductive, chemical properties, etc. Both reflect the original characteristic of filler: morphology, physical and chemical structures.

Commonly, filler is usually exploited for their “self properties” in composite. “Collaborative properties”, which decide the type of plastic which the filler could be incorporated, are often neglected and the focus is usually on filler treatment as well as on coupling agents.

Demonstrating for the exploitation of self properties is rubber toughening of epoxy and other brittle plastics. The study focused on the elasticity of rubber in order to enhance fracture resistance. Typical elastomers those are used for this system are liquid rubber butadiene-acrylonitrile (CTBN, ATBN and ETBN) (Chikhi et al., 2002; Robinette et al., 2004; Thomas et al., 2007). The toughening effect is achieved but there are some drawback of decreasing stiffness, strength and thermal properties of epoxy composites. In order to improve these drawbacks the introduction of high T_g

thermoplastic as a toughening agent such as polysulphone, phenylmaleimide, polystyrene, hydroxyl terminated poly (ether ether ketone) etc. are explored (Mimura et al., 2001; Giannotti et al., 2003; Francis et al., 2005; Hernandez et al., 2007; Gong et al., 2008). However, the toughening efficiency was lower compared to the liquid rubber modified epoxy.

The addition of preformed core-shell particles in the plastic by in-situ polymerization of monomer is exploited to partially surmount this difficulty (Duguet et al., 2000; Nguyen-Thuc and Abderrahim, 2002; Becu et al., 2002; Luna-Xavier et al., 2004; Tang et al., 2006; Dzunuzovic et al., 2007). The morphology and properties of core-shell particles can be tuned in advance, so that the composite could be prepared in predetermined morphology and independent of the curing process. Nevertheless, there is a drawback of limited size of core-shell particles (in the range of 100-500nm) (Woo & Hseih, 1998; Minami et al., 2005).

1.2 Multiporous hollow particles

In order to increase the contact area between matrix and filler, commonly the filler will be reduced in size such as from micron filler to nano-scale filler. The use of nano filler is normally challenging in term of obtaining good dispersion and to overcome favourable agglomeration. The other effects of nano filler are safety and health factors since nano filler is possible to be inhaled and can even cause endosmosis through human skin. Other material of higher surface area is hollow microsphere, which has been widely applied in packing system as packing material for chromatography column and spacer spheres for liquid crystal display (LCD), polymer-supported catalyst, polymer-immobilized extractant, templates of preparing porous inorganic microsphere, carrier of

enzymes and drugs (Omi et al. 1997). However, its utilization as reinforcing filler is less investigated.

The common method to produce hollow microspheres are alkali swelling procedure (ASP), dynamic swelling method (DSM), Shirasu porous glass (SPG) membrane technique, and water-in-oil-in-water (W/O/W) emulsion polymerization technique which involve the use of organic solvents or oil and using microfluidics (Shah et al., 2008). Blending of hollow microspheres with other polymer could be limited or less adherence. The use of supercritical carbon dioxide (SC CO_2) as a foaming agent to generate porous polymer materials was reported to avoid the solvent-removing processes, but the method needs high pressure vessel and high pressure pump. Based on the method of safe-assembling of phase separated polymer (SaPSeP) at the interphase of the droplets of SaPSeP, Minami et al. (2005) succeeded to synthesis cured epoxy resin particles having one hole at interface with water.

1.3 Problem statement

1.3.1 Common porous hollow particles

The microspheres have closed cell structure and possess fewer holes at the surface which make them not suitable for interlocking with matrix. The hollow structure sizes in these methods are quite small, the cell walls are also thin and these factors may interfere interlocking mechanism and subsequently results in a weak interlock. Moreover, the production process involves to oil and solvent, hence the interaction of the porous hollow particles and matrix could be weak. Inorganic microsphere usage is also reported and it works quite similar to common filler and the term of interlocking is not really obvious (Calisle et al., 2007).

1.3.2 Chemically induced phase separation

In all above systems, the toughening efficiency is strongly depended on chemically induced phase separation but it is difficult to control and obtain a stable the morphology of final toughened particles. It could be said the "collaborative properties" of these systems is weak and needed improvement. In these composites, polymer particles are firstly dispersed as filler in a continuous polymer matrix where polymer particles play a role to suppress the crack tip in the matrix via the aid of difference in hardness and toughness between filler and polymer matrix (Zhang et al., 2009). For example, general toughening plastic by using sphere shape particles are as follows, (i) delamination at interface between filler and matrix (Figure 1.1 (a)), and (ii) failure of the filler due to a break into the filler (Figure 1.1 (b)).

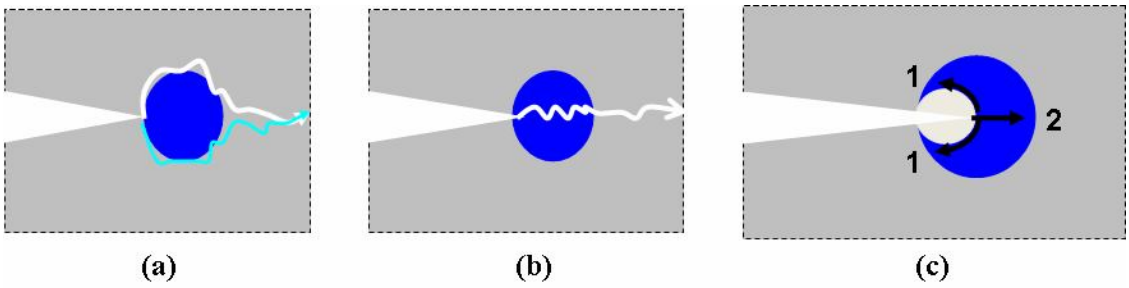


Figure 1.1 Problems of sphere shape filler dispersed in polymer matrix; (a) delamination and (b) failure of the filler. (c) New concept of interlocking mechanism, inner curve of the hole prevents delamination (arrow 1) and failure (arrow 2).

1.4 Porous hollow epoxy

In this study, a novel water based method is introduced to prepare micro epoxy particles having not only one but many holes (micro sizes) at the surface. The toughness and stiffness of epoxy particles can be obtained by varying the ratio of epoxy and polyamide. This method is relatively simple and environmental friendly because no

solvent is used and the possibility of production on a large scale is high. The presence of more than one hole in micro size is very promising since it has potential to be used as reinforcing fillers, which can be filled with matrix through interlocking mechanism. This advanced filler leads to a prospect of multiple function filler applied not only for epoxy matrix but also for other types of matrix such as elastomers and even for non-polymer matrix like ceramic and alumina. Besides interlocking application, the porous hollow epoxy can also be used as a drug or DNA carrier in bio-science.

The holes can be filled with matrix to form interlocking and consequently the composite properties were enhanced via this interlocking mechanism which is considered as a new and novel concept. The special characteristic of this filler incorporation in a polymer is that epoxy phase of the filler is cured and independent from curing process of the matrix. These particles are porous and hollow so that the morphology of dispersed epoxy into polymer will result in better dispersion and interaction composite material. The porous hollow epoxy exhibits better collaborative properties via its morphology and surface features. The interlocking mechanism that could happen is as suggested in Figure 1.1 (c) previously.

For porous hollow epoxy filled matrix, the interlocking mechanism expresses its reinforcement based on the type of polymer matrix. Possible failure of interlocking mechanism could be suggested as:

i. Pulling out but able to maintain interlocked morphology for such flexible and toughened elastomers. Pulling out but unable to maintain interlocked morphology with elongated features such found in flexible and fiber forming thermoplastic.

ii. No pulling out but neck breaking of the interlock such found in weak elastomers, brittle thermoplastic and thermoset.

iii. Breakage of porous hollow structure due to high adhesion between epoxy and matrix.

1.5 Objectives of the study

The objectives of the study are to produce the porous hollow epoxy particles by water-based method and propose the formation mechanism of porous hollow structure. The ability of porous hollow epoxy as filler is studied by preparing composites through common process such as casting, two-roll mill, internal mixer (Brabender, Haake), hot press, in-situ polymerization and sol-gel method. Through that, the interlocking practicability of porous hollow epoxy is proven with other type of polymers such as NR latex, elastomer (NR, ENR), thermoset (epoxy cured polyamine), thermoplastic (LLDPE, PS, PMMA) and inorganic (Silica). Furthermore, the effect of interlocking on mechanical properties and thermal properties of are investigated. The failure mode under tensile and tear of interlocking of porous hollow epoxy in different polymers are observed. Lastly, the effect of different particle size and porous hollow structure on in-situ polymerization and melt blending composite are studied.

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Fillers

2.1.1 Functions of filler in composites

The definition of filler in Handbook of filler (Wypych, 2000) is “Filler is a solid material capable of changing the physical and chemical properties of materials by surface interaction or its lack thereof and by its own physical characteristics”. From this definition, it could be suggested that filler works more than as an additive. The use of filler in a polymer matrix is very common in polymer composite in order to reduce the cost, reinforcement, alter the processing method. The choice of filler depends on the application of polymer. In fact, nowadays, the use of filler is not simply as the way to reduce cost but to obtain the specific properties of the composites. Properties of filler will be exploited via the combination of filler and plastic.

2.1.2 Type of fillers

There is some classification of fillers. The most common classification of fillers is according to their mineral origin and their chemical composition (mineral, glass, carbon black, organic, metal). Nowadays, more fillers are studied, synthesized and introduced to research and industry so the division of fillers which is based on filler characteristic could be more suitable. Fillers can also be divided based on their particles sizes (micro-sizes, nano-sizes), or their morphology (common shape, irregular, particles, fiber.). Fillers can be grouped in application through their properties such as mechanical, thermal, electrical, magnetic, fluorescence, opacity as

well as degradability, bio-degradable. This classification is more propagated nowadays in researches and industries.

2.1.3 Filler properties

The overall value of a filler is a complex function of intrinsic material characteristics, such as average particle size, particle shape, intrinsic strength, and chemical composition; of process-dependent factors, such as particle-size distribution surface chemistry, particle agglomeration, and bulk density; and of cost. Abrasion and hardness properties are also important for their impact on the wear and maintenance of processing and molding equipment (Mark, 2004). Here are some typical properties of a filler, which have influences on filler dispersion, loading and mechanical properties of composites (Wypych, 2000; Mark, 2004).

i. Chemical composition

Fillers can be inorganic or organic and of an established chemical composition. Filler can also be a single element, natural products, synthetics filler, mixtures of different materials in unknown proportions (waste and recycled materials), or materials of a proprietary composition.

ii. Physical state

Most of fillers are used in solid state or can be as a dispersed state. Filler can be in liquid state of monomer or solvent dissolved state which is used in the process of in-situ polymerization, sol-gel methods, rubber toughening plastic and polymer toughening plastic.

iii. Morphology of filler

Filler can have these morphologies such as spherical, cubical, irregular, block, plate, flake, fiber, mixtures of different shapes and also hollow or porous. The

shape of an individual particle has great impact on the flexural modulus, permeability, and flow behavior of a filled polymer. Spherical particles give the highest packing density, a uniform distribution of stress, increase melt and powder flow, and lower viscosity. Cubic and tabular shapes give good reinforcement and packing density. Dendritic particles have a very large surface area available for interaction. Flakes have large reflecting surfaces, facilitate orientation, and lower the permeability of liquids, gases and vapors. Elongated particles give superior reinforcement, reduce shrinkage and thermal expansion and facilitate thixotropic properties. Irregular particles may not possess special advantages but they are generally easier to make and are thus considered as inexpensive fillers.

iv. Particle size and aspect ratio

Filler size can range from a few nanometers to millimeters. Nano-filler is more focused recently because better electron microscopy equipment (SEM, TEM, AFM) are available. It could be said that sub-nano filler can be investigated in future whenever it can be evident and proven using laboratory equipments. Nanoparticles, with dimensions ranging up to 100 nm, deliver the strongest enhancements only when they are properly dispersed. Due to increases in both the surface area and the corresponding surface area to volume ratio with a reduction in filler particle size, finer particles are prone to agglomerate for the conservation of internal energy and are more difficult to be dispersed. The particle size is actually based on one dimension of the filler and the estimation is related to the determination methods themselves. Particle size determination is complicated by size distribution, the presence of particle associations, and the shape of particles. For those particles in irregular shape, it is difficult to express their dimensions. The method used for particle size determination (sieving, light scattering, microscopy) determines what

dimensional aspects are measured. For hollow filler particles, the dimension of holes and porous is essential for the interlocking application.

The aspect ratio, or the ratio of the longest length of particle to its thickness, is most commonly used to measure the shape of a filler particle. The aspect ratio of a sphere was the lowest and equal to 1.0. The aspect ratio increases with a filler's shape progresses from a sphere to a block, to a plate, or to a flake. The filler loading content and dispersion depends on this aspect ratio.

v. Particle size distribution

Particle size distribution of filler can be monodisperse, designed mixture of sizes, Gaussian distribution or irregular distribution. In polymer composites, the particle size distribution of the filler has influence on viscosity and on loading content of filler during incorporation. In some plastics, a certain stress distribution is required and, in such cases, monodisperse, spherical particles are best. Changes to the particle size distribution will change the undertone of the pigment allowing a system to be tailored to the requirements. Certain grades may be capable of providing optical brightening or of masking the yellow color.

vi. Surface area

Surface area is a very important parameter of filler. Surface area value varies depending on the measurement methods. BET is the reasonable methodology for surface area measurement. The surface area depends on particle size, morphology and porosity. The specific surface area determines the contact surface between filler and matrix and influences significantly mechanical properties of the composites (Pukanzsky, 1996).

vii. Wetting and coupling properties

Wetting and dispersion of filler are critically depended on the chemical compatibility between filler surface and matrix, which affects directly to physical performance of filled polymer. According to water affinity, filler surfaces are usually classified as hydrophilic or hydrophobic. Mineral fillers can be coated or chemically treated with hydrophobic wetting agents to modify their surface chemistry to aid their dispersion in nonpolar polymer. The modification with wetting agents also restricts agglomeration of filler so allow for higher filler loadings with lower viscosities during filler incorporation. The wettability can also be estimated by the contact angle measured between a drop of water or oil and the filler surface.

viii. Hardness

The effect of filler to polymer hardness depends on the interaction between filler and polymer. Soft filler (such as rubbers toughen rigid plastic) is able to enhance fracture toughness.

ix. Mechanical properties

Strong mechanical filler could prevent a failure of tear or break filler so the mechanical properties of composites will depend on interaction of filler and matrix.

x. Other properties

pH of filler also affects the dispersion in polymer. The high particle – particle interaction and attraction will lead agglomeration and causes a poor dispersion of filler in matrix. The thermal conductivity of filler and its concentration are the main parameters determining the thermal conductivity of composite. Thermal expansion coefficient affects the dimensional stability of composites. Thermal expansion can be used as simple method of verifying the adhesion between the filler and the matrix. If the adhesion is poor the composite will have high thermal expansion. Beside that, the

blending processing is influenced by the thermal conductivity of filler, especial organic filler and its melting temperature (Wypych, 2000).

In general, these properties of filler are essential to take into account for synthesis of a new filler for polymer. Depending on the desired properties of composites, the selected properties of filler can be tailored. The focus is necessary not only on the enhanced properties (self properties) but also the interaction of filler to matrix (collaborative properties). In this study, interaction of filler is improved by the increase in surface area and the introduction of the new interlocking mechanism, which is achieved by exploiting the porous hollow structure of the produced filler.

2.1.4 Interactions

The properties of composites are critically dependent on the interface between the filler and the matrix polymer. The type of interface depends on the character of the interaction which can be either physical or chemical in nature. Both types of interactions contribute differently to the reinforcement of polymeric materials. Formation of chemical bonds in filled materials generates enhanced physical properties. An interfacial bond improves interlaminar adhesion, delamination resistance, fatigue resistance, and corrosion resistance. These properties are dependent on shape, size and functional group distribution of filler. The filler surface acts as a template for interface formation which allows the reactivity of the filler surface to come into play. Morphology of filler decides the surface area of filler, which can be in the form of spherical, cubical, block, flake, fiber (Wypych, 2000). There are two important factors in filler composites which are dispersion of filler in matrix and the interaction between them. Interaction is a complex process involving:

- A chemical reaction between the filler and matrix materials
- Physical interaction (van der Waals forces and hydrogen bonding)
- Changes in morphology of interacting components
- Mechanical interlocking

These processes modify surface layers of both interacting materials (filler and matrix) and form an interphase which differs in properties from the bulk matrix. The formation of the interphase is responsible for changes in the physical and mechanical properties of filled materials and usually improves material reinforcement.

It is suggested that three models of interaction between the surface of the filler and the matrix, which are mainly based on the types of fillers used. The first model is according to the typical report of Tsagaropoulos & Eisenberg (1995), which is shown in Figure 2.1. The filler particles of lower or about 10 wt% is surrounded by a tightly bound polymer covered by a layer of loosely bound chains. As the loading increases, the areas of loosely bound polymer begin to overlap, consisting the entire matrix to be influenced by the filler. If filler loading is high, there is little space left for loosely bound polymer and the participation of the layers of tightly bound polymer increases. At different filler loadings, a change in the interaction mechanism is likely to occur.

The second model of interaction between the surface of the filler and the matrix is the rubber chain attaches to carbon black (Figure 2.2). The rubber chain can be attached at single points (a), multiple points (b) and connected two or more carbon black particles. Reactive functional groups can be positioned in the middle of chain or at its ends and the reactions may involve chain segment or terminal group.

The third model is the report from Datta et al. (1996). The authors proposed a model of chemical interactions for a system of carbon black and maleated EPDM as

shown in Figure 2.3. The links could be hydrogen bonding and covalent bonding, which are characterized by the attachment of filler particles to the chain. Because the rubber is crosslinked, there is more opportunity for it to form interaction.

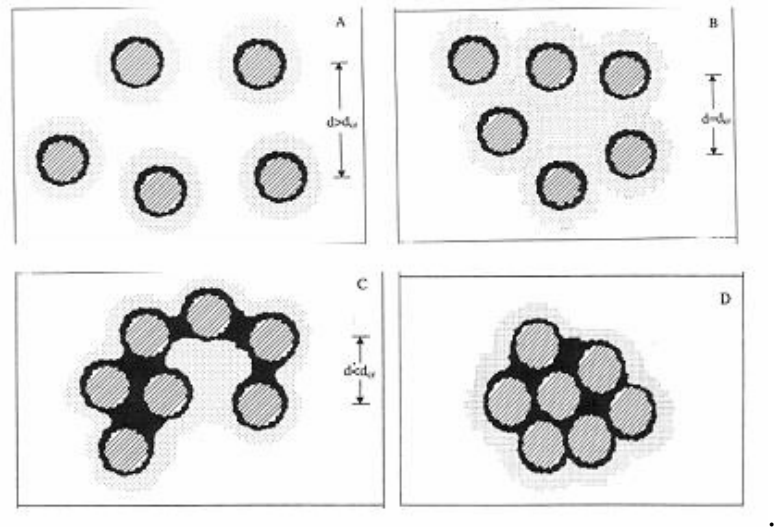


Figure 2.1. Schematic model of the morphological transformations in filled polymers, occurring as the silica content increases from less than 10 wt % (A), to ca. 10 wt % (B), to over 20 wt % (C), to over 50 wt % (D). The line-shaded areas are the silica particles, while the black areas correspond to tightly bound polymer and the gray areas to loosely hound polymer. (Tsagaropoulos & Eisenberg, 1995).

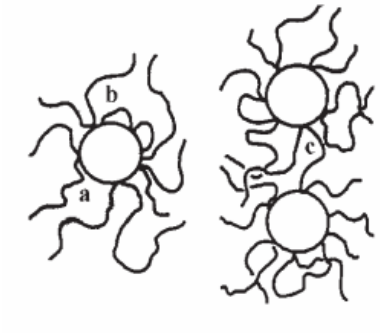


Figure 2.2. The concept of segmental interaction with carbon black surface (Wolff et al., 1996)

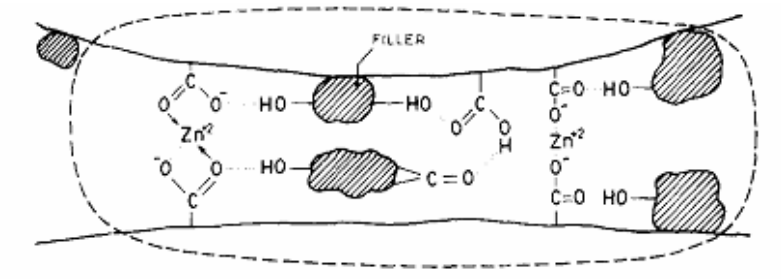


Figure 2.3 Probable mechanism of interaction between filler particles and ionic groups in the restricted mobility region (Datta et al., 1996)

The interaction of filler and matrix is usually improved by using coupling agents which are suitable for both filler and matrix. The use of smaller particles is also preferred to increase the contact area between matrix and filler, commonly the size of filler will be reduced such as from micron filler to nano-scale filler.

. The most common nano-filler is montmorillonite clay which has a crystal structure of layered silicate. For such filler, it required a modification on the clay so that the composites could obtain nano structure of filler and have a good dispersion of filler. If energetically favorable interactions exist between the modified silicate and the polymer, then the polymer chains can be inserted between the silicate layers, further increasing the interlayer spacing and leading to an ordered multilayer with a repeat distance of a few nanometers. If the polymer and the silicate are not compatible, agglomerates of layered silicate surrounded by polymer are formed. Thus, in the use of such clays as fillers in polymer systems, three general types of composite materials may be obtained (Figure 2.4): (a) conventional composites containing clay tactoids of stacked layers in a coplanar orientation associated in aggregates and agglomerates dispersed as a segregated phase, (b) intercalated nanocomposites, and (c) exfoliated nanocomposites (Joly et al., 2002).

Figure 2.4. Schematic representation of the three types of polymer-clay composites (Joly et al., 2002)

For mechanical interlocking, Gorl et al. (1996), who investigated the size of voids in fumed silica in its original form and after compounding with rubber, suggest that the increase in the size of pores depended on the conditions of mixing and on the formulation of rubber. Reinforcement required the initial size of silica pores to be large enough to allow penetration by rubber chains.

Interlocking of polymer matrix and filler is rather new, we propose the schematic of how the polymer chains attach to filler in Figure 2.5. In general, interlocking is a macroscopic phenomenon, which actually consists of common interaction of polymer chains to filler surface. Here, the enhancement comes from higher surface area of filler as well as the dovetailing effect which is similar to snap button mechanism.

Figure 2.5 The schematic of polymer chains interlocked in porous hollow particle

2.1.5 Porous hollow particles

As high surface area materials, hollow microspheres have been widely applied as packing materials for column chromatography and spacer spheres for liquid crystal display (LCD), polymer-supported catalysts, polymer-immobilized extractants, templates of preparing porous inorganic microspheres, and carriers of enzymes and drugs (Omi et al. 1997). However, the use of hollow microperes as reinforcing filler is not widely investigated.

There are numerous reports to produce porous hollow particles by various methods. The common methods to produce hollow microspheres are alkali swelling

procedure (ASP) , dynamic swelling method (DSM) (Okubo et al., 1996), Shirasu porous glass (SPG) membrane technique (Omi et al., 2000) and water-in-oil-in-water (W/O/W) emulsion polymerization technique which involve the use of organic solvents or oil (Kim et al., 1999, Kim et al., 2003). Lee et al. (2008) reported a multihollow structure of poly(methyl methacrylate)/silver nanocomposite microspheres prepared by suspension polymerization in the presence of dual dispersion agents. The hollow particles obtained with different hole sizes which are dependent on the concentration of surfactant Arlacel P135.

Alkali/cooling method to produce multihollow polymer particles was proposed by Okubo et al. (1996 & 1997). Styrene with 10wt% of methacrylic acids – MAA was allowed to emulsion polymerize at 70^{o}C. The emulsion of over 95% conversion was diluted and adjusted to pH 12.0 with alkali aqueous solution and then was heated by dipping in oil bath at 150^{o}C for 3h. After the treatment, each emulsion was cooled under the room temperature. The alkali treatment could react with trapped MAA to produce holes on the particles. The holes were observed under TEM as closed holes and in nano size (Figure 2.6)

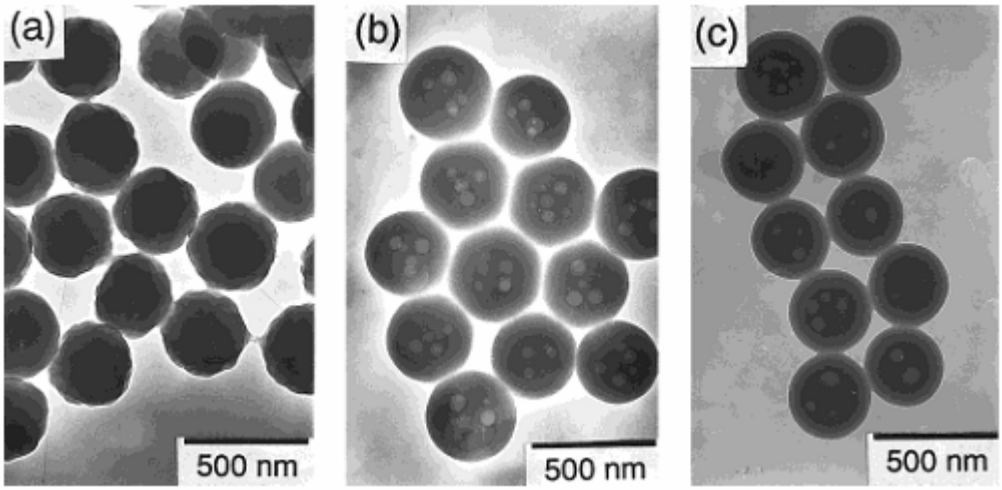


Figure 2.6 TEM photographs of P(S-MAA) (MAA content, 10 mol %) particles before (a) and after (b) and (c) treated at 150^{o}C for 3h at initial pH value of 10.5 adjusted with NH_4OH (b) and ethanolamine (c) (Okubo et al., 1997).

Hong et al. (2007) reported a preparation of porous/hollow phenolic particles by suspension polymerization from a resol, water-soluble phenolic resin in a multiple emulsion system oil-in-water-in-oil (O/W/O) (Figure 2.7). The water-soluble phenolic resin was synthesized via condensation of phenol and formaldehyde with an alkaline catalyst to have a 50wt% resol precursor solution. Rapeseed oil, OP10 and resol solution were mixed in the homogeneous solution to get the O/W pre-emulsion, which was dropped slowly into the reaction kettle containing rapeseed oil and Span 80 (to obtain O/W/O system). The polymerization was carried out continuously at 130^{o}C for 4h in N_2 atmosphere. The porous particles obtained were spherical particles contained voids or bubbles. These are closed voids and porous particles looked similar to closed cell.

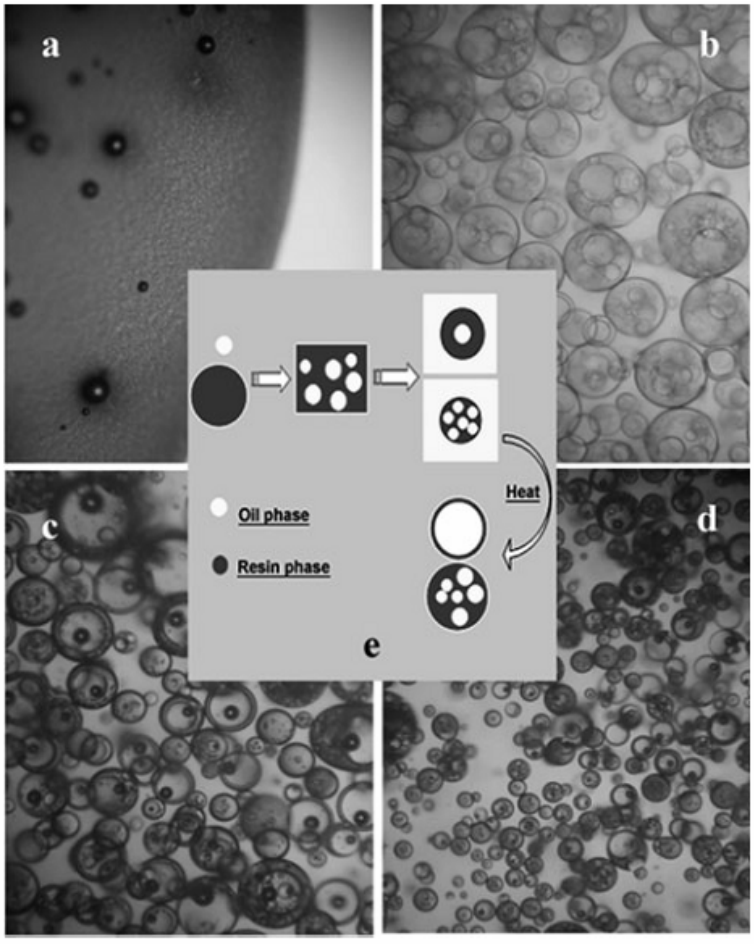


Figure 2.7 OM micrographs of the formation of phenolic resin particles (X100) and the scheme of formation of porous-hollow particles (Hong et al., 2007)

Hong et al. (2006) fabricated PMMA/butyl acrylate – BA porous microsphere through the emulsion polymerization in company with a phase inversion process. Mixture of monomer of MMA/BA, initiator and additives was charged a round-bottomed reactor equipped with a mechanical stirrer, a reflux condenser, thermocouples, and an N_2 inlet system. Solution of sodium hydrogen phosphate (Na_2HPO_4) sodium dodecyl benzene sulfonate (SDBS), poly (vinyl alcohol) and water was dropped slowly into the reactor at a given agitation speed to drive phase inversion. Then the polymerization was carried out continuously at 65°C for 4h. The porous particle obtained was similar to an open foam particle in spherical, which have numerous of connected holes and thin side walls (Figure 2.8).

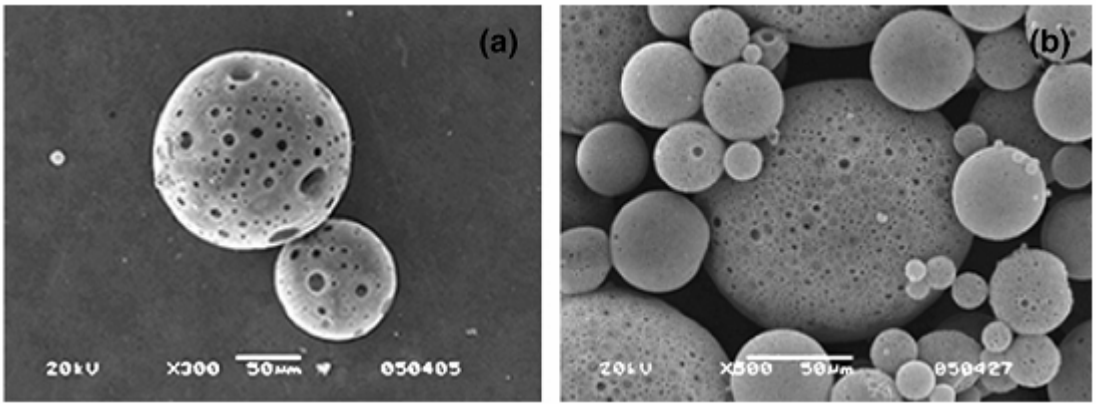


Figure 2.8 SEM micrographs of two type of multiporous hollow particles (Hong et al., 2006)

Kim et al. (2003) described the methodology of production of multihollow polymer microcapsules by water-in-oil-in-water emulsion polymerization. W/O/W emulsion polymerization was carried out by modifying the two-step emulsion procedure. First, a W/O emulsion was prepared as follows aqueous solution containing a model water-soluble ingredient was dropped into an oil phase composed of MMA, EGDMA monomer and additives. Then, the water/oil mixture was homogenized. The W/O emulsion prepared was a milky viscous phase. Second, the

W/O emulsion was re-dispersed by homogenizing it mildly in 1wt% PVA aqueous solution, obtaining finally a stable W/O/W emulsion. Right after the preparation of the W/O/W emulsion, the emulsion was transferred into a double-walled glass reactor to polymerize at 60^{o}C for 10h under N_2 inlet system. The inhibition of polymerization in the aqueous phase is required. As shown in Figure 2.9, the particles were porous of multi close holes and no holes present on particles surface, so the application should not applicable for interlocking mechanism.

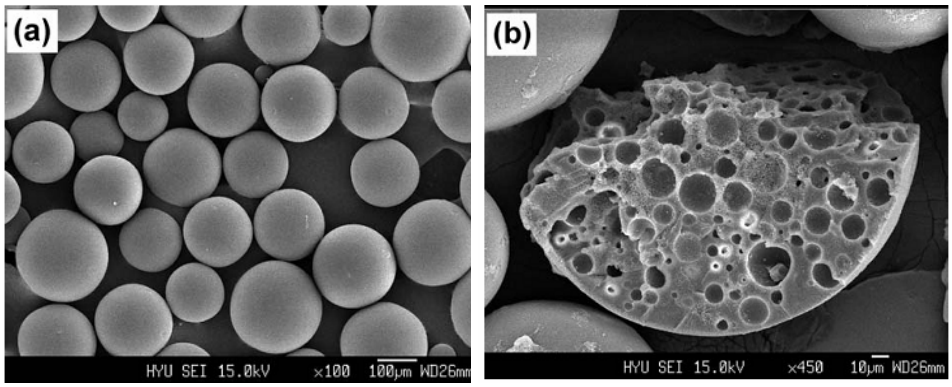


Figure 2.9 Scanning electron microscope photographs of multihollow poly(methyl methacrylate) (PMMA) microcapsules cross-linked with 50 wt% ethylene glycol dimethacrylate (EGDMA): a surface image and b inner phase image. The calculated loading yield of monosodium phosphate (MSP) in the microcapsules was 5% (Kim et al., 2003)

Most studies of W/O/W emulsions have dealt with the stabilization of active ingredients and their sustained-release properties. A serious problem can be found in that there have been few works that satisfy the requirements for wide application. The reasons for this are their intrinsic thermodynamic instability and low active ingredient entrapment efficacy. To overcome all those failures of W/O/W emulsions, a stable W/O/W is essential.

The use of supercritical carbon dioxide (SC CO_2) (Sun et al., 2004, Huang et al., 2007) as a foaming agent to generate porous polymer materials was reported to avoid the solvent-removing processes, but the method needs to utilize high pressure vessel and high pressure pump.

Recently, Shah and his colleagues (2008) reviewed and introduced the designer emulsions using microfluidics. The glass capillary devices were used to generate single, double, and higher order emulsions which can serve as ideal templates for producing well-defined particles and functional vesicles. The method is needed to engineer pathways to scale up the production.

All the above methods exploit the entrapment of the other unmingled components in monomer phase. The polymerization and further removing process are used to form hollow structure. All these methods also bring some drawbacks: complex treatment procedures and industrial waste, which lead to much time wasting and consumption. The membrane technique to produce microspheres through polymerization of the monomer emulsion using Shirasu porous glass (SPG) is complex method.

Liu et al. (2007) produced micro hollow microspheres by suspension polymerization of Styrene-DEGDA (diethylene glycol diacrylate) with petroleum ether (90 – 120^{o}C), but there is single hole on the particles. The possibility of production in large scale is not promising. The microspheres are closed cell and have less micron size holes at the surface which make them not suitable for interlocking with matrix. The hole sizes in these methods are quite small, and the cell walls are also thin which subsequently restricts the formation of interlock and results in weak interlocking. Moreover, blending of these hollow microspheres with other polymer could be limited or low adherence due to the oil phase.

Inorganic microspheres are also reported by several workers, and they were quite similar to common filler and the term of interlocking is not really obvious (Kim et al., 2001, Liang et al., 2007, Calisle et al., 2007, Liu et al., 2009). Hakido et al. (2005) reported the synthesis of hollow calcium carbonate by bubble templating

method. Hollow $CaCO_3$ particles were produced by using bubble as template via passing CO_2 bubbles into calcium chloride ($CaCl_2$) solution in the presence of ammonia (NH_3) at 27^oC. The CO_2 bubble is not only the reactive material, but also the template for the hollow particles. The newly-formed primary particles were attached to the bubbles and formed a solid shell. After filtering and drying, hollow $CaCO_3$ particles were obtained. This hollow $CaCO_3$ is similar to a $CaCO_3$ balloon and the broken particle would show an empty core as seen in Figure 2.10b.

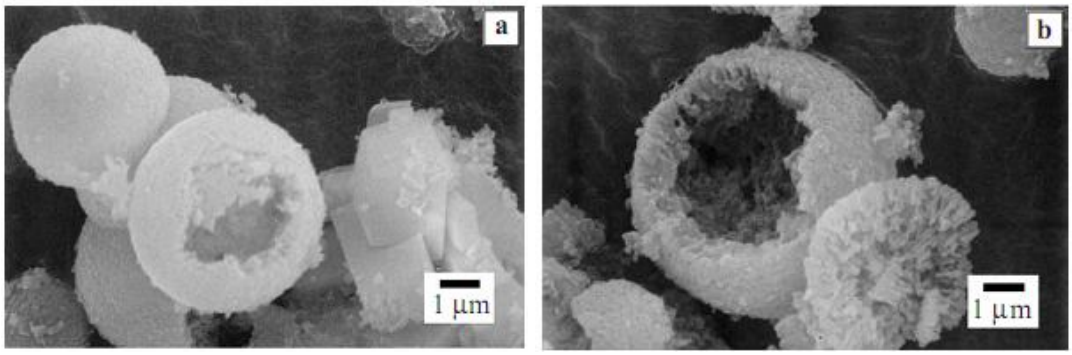


Figure 2.10 SEM micrographs of $CaCO_3$ precipitates at pH 9.8 (Hakido et al., 2005)

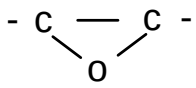
Based on the method of safe-assembling of phase separated polymer at the interphase of the droplets SaPSeP, Minami et al. (2005) succeeded to synthesise cured epoxy resin particles having one hollow at interface with water. The presence of polystyrene (PS) dissolving in epoxy/diamine/toluene droplets are exploited to promote the phase separation of the epoxy reacted with the diamine. PS needs to be prepared by solution polymerization with 2,2'-azobisisobuthyronitrile as initiator. When the PS did not dissolve in the droplets, no hollow particles were obtained. There were certain minimum values of the PS content and its molecular weight to obtain the hollow particles. In this case, polyvinyl (vinyl alcohol) (PVA) is also needed as a colloidal stabilizer.

In the present work, a novel water based method is introduced to prepare micro epoxy particles having not only one but many holes (micron sizes) at the surface. The toughness and stiffness of epoxy particles can be obtained by varing the ratio of epoxy and polyamide (Du, 2003). This method is so simple and environmental friendly because no solvent is used and the possibility of production on a large scale is high. The presence of more than one hole in micron size is very promising since it has potential to be used as reinforcing fillers, which can be filled with matrix through interlocking mechanism. This advanced filler leads to a prospect of multi function filler applied not only for epoxy matrix but also for other types of matrices such as elastomers, thermoplastic and even for non-polymer matrices like ceramic and alumina. Besides interlocking application, porous hollow epoxy can also use as a drug or DNA carrier in bio-science but with a caution of bio-degradable.

2.2 Epoxy and Polyamide

2.2.1 Epoxy

Epoxies are thermoset resins and are characterized by a three-membered oxide ring known as epoxy, epoxide, oxirane or ethoxyline group:



The epoxy ring is susceptible to attack from a wide variety of substances to form the crosslinked three dimensional networks in the end product. There are many types of epoxy resins such as: epichlorohydrin-bisphenol A, phenoxy resins, epoxy novolac resin, halogenated epoxy resin, hydrogenated bisphenol A resin, Among them, liquid epichlorohydrin-bis phenol A resin is the most important resin and have wide applications due to the low viscosity and easy processing. As can be seen from

its name, epcihlorohydrin-bisphenol A is the product of the condensation of epichlorohydrin (ECH) with diphenylolpropan (DPP) which is also called bisphenol A in the presence of NaOH as catalyst. Epichlorohydrin behaves as a difunctional monomer, the epoxide group can be opened by hydroxyl group of bisphenol and the halohydrin can be dehydrohalogenated by alkali. The ratio of epichlorohydrin and bisphenol A has an effect on the average molecular weight of the liquid resin (Adams & Gannon, 1985). Uncured liquid epoxy is mainly characterized by the epoxy content, viscosity, color, density, hydrolysable chlorine and volatile content. The epoxy content is expressed as weight per epoxide (wpe) or epoxide equivalent weight (eew), which is defined as the weight in gram which contains one gram equivalent of epoxide.

2.2.2 Curing with polyamide

Vegetable oil-polyamide resins are also called Versamids. Versamids were introduced in the early 1950's, have dark colour, ranging from viscous liquids to brittle resins and with varying solubility. These polyamides have found usage as hardeners-cum-flexibilisers for epoxy resin (Brydson, 1975). Polyamide Versamids are condensation products of fatty dibasic acid (C-13, C-19, C-21 and C-36) and di-polyfunctional amines. Most of reactive polyamide is prepared from dimer acids, and diethylenetriamine (DETA).

Dimer acids (polymerized vegetable oil acids) are usually prepared from tall oil fatty acids (TOFAS). The reaction that formed dimer acids occurs under heating, steam pressure and chemical catalyst. The structure of dimer acid is shown in Figure 2.11 (Adams & Gannon, 1985).